

Research on a temporary plugging agent based on polymer gel for reservoir acidification

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Abstract A temporary plugging agent based on polymer gel was successfully prepared for temporary plugging in acidizing treatment. The gelation time, gel-breaking time, viscosity changes, temporary plugging capacity, and permeability recovery capacity were investigated. Increasing the polymer and cross-linker concentration reduced the gelation time of the polymer gel and temporary plugging agent, but caused difficulties in breaking the temporary plugging agent. Ammonium persulfate (APS) could be the driving force for the differences of gelation time between the polymer gel and temporary plugging agent. Additionally, increasing APS concentration made the temporary plugging agent break easily. Viscosity changes are the most important feature of a temporary plugging agent. According to the viscosity changes, the whole process can be divided into two major stages: the cross-linking reaction stage and the degradation reaction stage. The temporary plugging agent had a good plugging capacity which could effectively plug the high permeability zones. By temporary plugging, the pollution near wellbore was removed without damaging non-target zones. As a result, the permeability of the low permeability zones was greatly improved, and the permeability of the high permeability zones was effectively recovered.

Keywords Temporary plugging agent · Polymer gel · Temporary plugging capacity · Reservoir acidification

Introduction

A reduction in formation permeability or hydraulic conductivity has attracted much concern in the oilfield development stage (Vaidya and Fogler 1990; Mohan et al. 1993; Gasda et al. 2013). The loss of permeability and poor hydraulic conductivity usually lead to serious heterogeneity and low fluid production, and thus effect oil production. It is commonly referred to as formation damage in an oilfield. Generally, solid-phase invasion, fines migration, scale formation, and water sensitivity (Chen and Dai 2005; Wu et al. 2007; Buchsteiner 1993; Sadeghazad and Beiranvand 2003) can cause pollution and plugging near the wellbore which has adverse effects on oil production. Acidizing treatment is one of the most important techniques that has been utilized in attempting to remove the pollution and recover formation permeability (King 1986; Wahib et al. 2010; Buijse et al. 2004; Pournik et al. 2011). Acidizing treatment involves an injection of acidizing solution, such as HF, HCl, or HBF₄ into the formation which can react with clay particles, carbonate, and FeS, and thus, the permeability near the wellbore is recovered.

However, injection of an acidizing solution into target zones without damaging non-target zones (high permeability zones) is a key issue. Temporary plugging agents are usually used to plug the high permeability zones in the acidizing process. Because of temporary plugging, the acid will tend to flow into low permeability zones and remove pollution, thus reducing existing permeability disparities. Polymers, particles, and foam are selected as temporary agents in the acidizing process (Alghazal 2012; Dorman and Udvary 1996; Himes et al. 1990; Thompson and Gdanski 1993). But the viscosity of a polymer is greatly reduced when used in a high salinity and temperature reservoir which confines its further application. Particles

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are a good temporary plugging agent in oilfield applications, but the injection volume is usually large. In addition, the plugging capacity of particles significantly decreases when swelled in the formation. Foam is easy deforming when dispersed in high concentrations of calcium and magnesium ion solutions. To overcome these problems, a temporary plugging agent based on a polymer gel was prepared, for the advantages of cost effective, easily broken, controllable gelation time, and adjustable strength. In this study, an environmentally friendly organic chromium cross-linker and anionic polymer were used to prepare the temporary agent. The gelation performance, gel-breaking performance, viscosity changes in the cross-linking reaction stage and degradation stage, temporary plugging capacity, permeability recovery, and temporary mechanism were systematically studied. Through laboratory experiments, we expect the work can serve as a reference for understanding this temporary plugging agent and become applicable for temporary plugging in the acidizing process.

Materials and methods

Materials

The anionic polymer and organic chromium cross-linker were provided by Yuguang Co. Ltd. China. The hydrolysis degree and molecular weight of the anionic polymer were 20 % and 12,000,000 g/mol, respectively. Ammonium persulfate (APS) was analytical reagent grade and purchased from Guo Guang Co. Ltd. China. The brine salinity used in all experiments was 3.37×10^4 mg/L (Ca^{2+} : 357.6 mg/L; Mg^{2+} : 1115.4 mg/L). The acidizing solution, containing 12 % HCl, 0.5 % corrosion inhibitor, 6 % ferric ion stabilizer, and 0.5 % clay stabilizer, was prepared in our laboratory, and the corrosion rate was more than 62 % after 10 h.

Methods

Gelation time and gel-breaking time

The gel strength code method (Sydansk and Argabright 1987) was used to determine gelation time and gel-

breaking time. During the gelation progress, the temporary plugging agent was sealed in an ampoule, and the cross-linking reaction was initiated at 65 °C in an oven. The ampoule was inverted at frequent intervals to observe gel formation, and the gelation time was noted as the time when the gel strength did not change. Sequentially, the temporary plugging agent was kept in the oven until the solution freely flowed in the ampoule, and the time was recorded as the gel-breaking time.

Rheological measurements

A Haake Rheostree RS75 rheometer was used to investigate the viscosity changes of the temporary plugging agent in the cross-linking process and degradation process. The shear rate was fixed at 1/s at 65 °C with a concentric cylinder mode.

Single sand-pack experiments

Single sand-pack experiments were carried out to evaluate the plugging capacity and permeability recovery capacity of the temporary plugging agent. The experimental flow chart is shown in Fig. 1. Sand-packs 20 cm in length and 2.5 cm in diameter with different permeabilities were used in all experiments. When conducting this experiment, 0.3 pore volume (PV) of the temporary plugging agent was injected into the sand-pack. Then the sand-pack was placed at 65 °C until the polymer gel was formed. Sequentially, water flooding was conducted at certain times until the pressure reached a stable condition. In this process, the pressure was recorded as p_i and the permeability was calculated as k_i . In single sand-pack experiments, the plugging rate and resistance factor which were used to characterize the plugging capacity of the temporary plugging agent are represented by Eqs. (1) and (2).

$$E = ((k_0 - k_i)/k_0) \times 100\% \quad (1)$$

$$F_{RR} = p_i/p_0, \quad (2)$$

where E and F_{RR} are the plugging rate and residual resistance factor, respectively; k_0 and p_0 are the initial permeability and pressure before injection of temporary plugging

Fig. 1 Flow chart of single sand-pack experiment

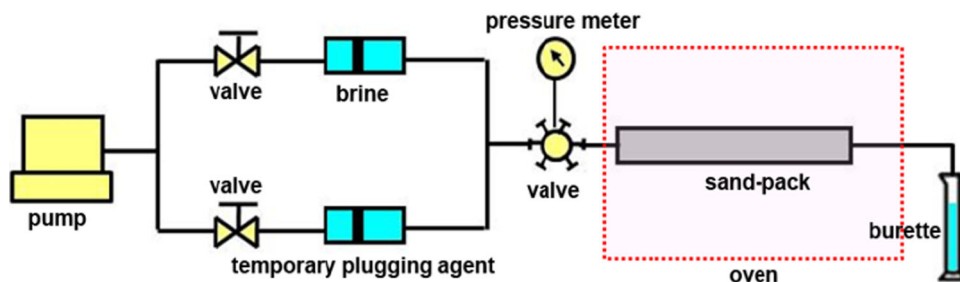
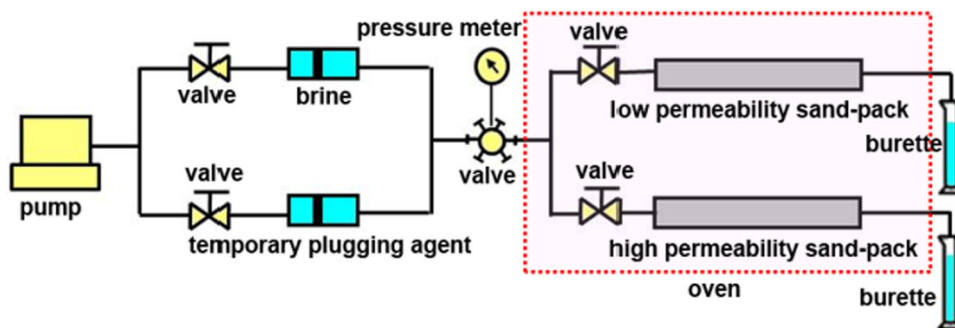


Fig. 2 Flow chart of parallel sand-pack experiment

agent, respectively; and k_i and p_i are the permeability and pressure in the i stage, respectively.

In addition, the permeability recovery rate was used to characterize the permeability recovery capacity of the temporary plugging agent by Eq. (3).

$$\sigma = (k_1/k_0) \times 100\%, \quad (3)$$

where σ is the permeability recovery rate, k_0 is the initial permeability before injection of the temporary plugging agent, and k_1 is the permeability in the last stage.

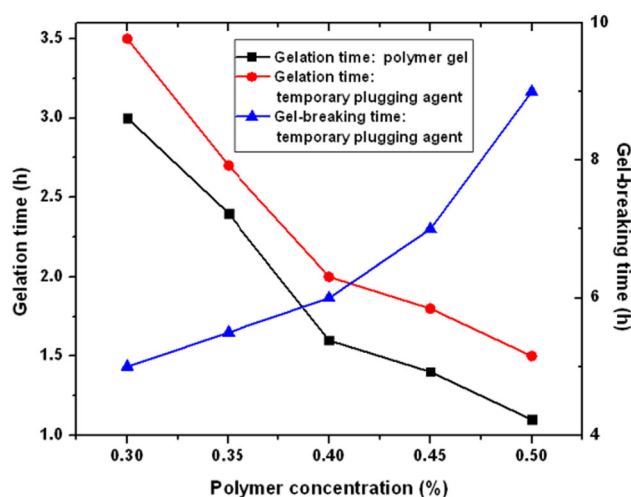
Parallel sand-pack experiments

Parallel sand-pack experiments were carried out to evaluate the temporary plugging capacity and permeability recovery capacity of the temporary plugging agent in the acidizing process. The experimental flow chart is shown in Fig. 2. A high permeability sand-pack and a low permeability sand-pack (20 cm in length and 2.5 cm in diameter) are used to simulate a heterogeneous formation in experiments. When conducting this experiment, scale samples were milled into 100–200 mesh and uniformly mixed with 30–60 mesh of sand in a mass ratio of 1:2, and then the mixture was filled into the sand-packs. In the process, 0.3 PV of temporary plugging agent was injected into the sand-packs. Then, the sand-pack was placed at 65 °C until the polymer gel formed. Sequentially, 4.0 PV of acidizing solution was injected into the sand-packs. Finally, water flooding was conducted until the pressure and produced fluid reached a stable condition. The pressure and produced fluid were recorded to characterize the temporary plugging capacity and permeability recovery capacity.

Results and discussion

Effect of polymer concentration

The polymer concentration was critical for the performance of the temporary plugging agent. It directly affected gelation time and gel-breaking time which further affected

**Fig. 3** Effect of polymer concentration on gelation time and gel-breaking time

plugging capacity and acidizing results in the formation. In the experiment, the cross-linker and APS concentration were, respectively, set at 0.4 and 0.01 %, while the polymer concentration varied from 0.3 to 0.5 %. Figure 3 shows that the gelation time of the polymer gel temporary plugging agent significantly decreased when polymer concentration increased, whereas the gel-breaking time increased from 1.5 to 3.5 h which indicates that increasing the polymer concentration causes difficulties in breaking the gel. A high polymer concentration provides more carboxylate groups ($-\text{COO}^-$) which are converted to a multi-core hydroxyl bridge ligand of Cr(III) ions by cross-linking reaction (Zhao et al. 2014). Therefore, the gelation time decreased with an increased polymer concentration. However, the gelation time was different when adding APS into gelation solution. APS is very unstable and can release oxygen when heated. The oxygen is more able to attack the carbonyl groups of the polymer. As heating continues, the carbonyl groups are further oxidized to break the polymer chain and reduce polymer molecular weight, and thereby decreases the cross-linking rate. The degradation and cross-linking reaction were simultaneously carried out in a

temporary plugging solution. In the whole process, the cross-linking reaction played a major role before gelling, while the degradation reaction mainly occurred after gelling. Therefore, the temporary plugging agent based on a polymer gel had a longer gelation time.

Effect of cross-linker concentration

A polymer is the skeleton in the gel structure, while the cross-linker is a bridge agent which brings polymer molecules together. Therefore, the cross-linker also plays a key role in the gelation process. In this experiment, the polymer and APS concentration were, respectively, set at 0.4 and 0.01 %, while the cross-linker concentration varied from 0.3 to 0.7 %. Figure 4 shows that both the gelation time and gel-breaking time increased with the cross-linker concentration. A high cross-linker concentration caused more multi-core hydroxyl bridge ligands of Cr(III) ions which enhanced cross-linking chances with carboxylate groups in solution; thereby, the cross-linking reaction was accelerated. Due to the APS in the solution, the generated oxygen caused adverse effects on the gelation process. As a result, the temporary plugging agent had a longer gelation time than the polymer gel. Additionally, the higher the cross-linker concentration was, the stronger the gel structure was. This caused difficulties for gel-breaking, and increased the gel-breaking time.

Effect of APS concentration

APS directly decides the plugging capacity of the temporary plugging agent. If the APS concentration is too low, the temporary plugging agent will still plug high permeability channels in the non-target zones after acidizing treatment. This can bring about secondary damage to the

formation. On the contrary, a high APS concentration will cause an uncross-linked temporary plugging agent which leads to a failed treatment. In the experiment, different levels of APS concentration were added to the solution (0.4 % polymer + 0.4 % cross-linker). Figure 5 shows that the gelation time increased but the gel-breaking time decreased with the APS concentration. A high APS concentration will provide more oxygen in solution which can easily attack the polymer bonds, and thus decrease polymer molecular weight. Therefore, the gelation time increases and gel-breaking time significantly decreases.

Viscosity changes of the temporary plugging agent in the cross-linking process and degradation process

The viscosity changes of the temporary plugging agent are a characteristic feature in the cross-linking process and degradation process. Thus, it is important to investigate viscosity changes that can help in gaining a better understanding of the cross-linking and degradation mechanism. Figure 6 shows viscosity changes of the temporary plugging agent (0.4 % polymer + 0.4 % cross-linker + 0.01 % APS) in the whole process at 65 °C. As shown in Fig. 6, the viscosity initially slowly increased. Then, the viscosity rapidly increased and finally became stable, indicating gelation. The viscosity eventually reached 8859.78 mPa s, and a high strength of bulk gel was formed after 2 h (Fig. 7a). However, the viscosity gradually decreased and eventually reached 2.68 mPa s, indicating that the temporary plugging agent was completely degraded (Fig. 7b, c). The photos in Fig. 7 also confirm the viscosity changes of the temporary plugging agent. Considering the viscosity changes in the process, the whole process can be divided into two successive stages: the cross-linking reaction stage and the degradation reaction stage.

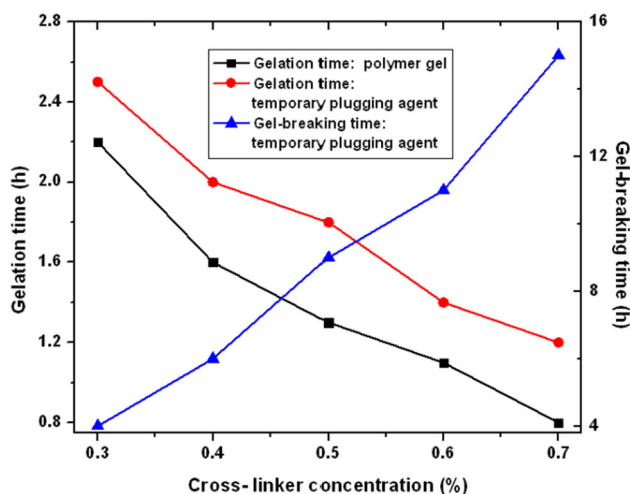


Fig. 4 Effect of cross-linker concentration on gelation time and gel-breaking time

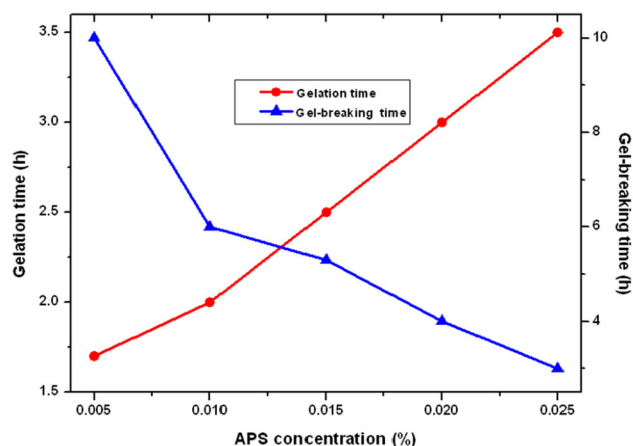


Fig. 5 Effect of APS concentration on gelation time and gel-breaking time

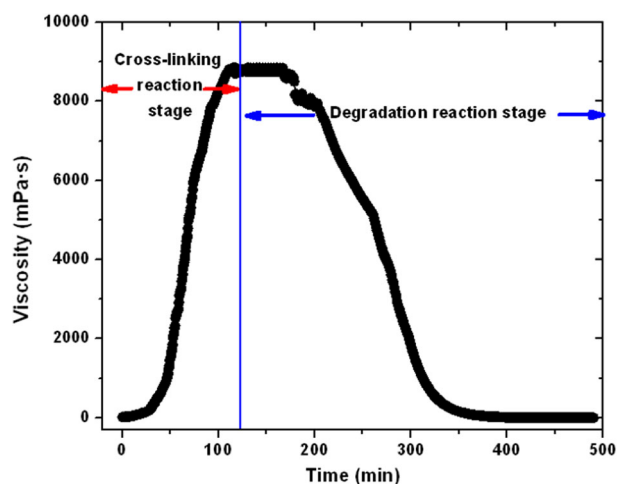


Fig. 6 Viscosity changes in cross-linking and degradation processes

Stage I: The cross-linking reaction stage. Figure 8 further shows viscosity changes in this stage. According to viscosity changes in the cross-linking reaction process, it can also be divided into three successive steps: the induction period, the rapid cross-linking period, and the stabilization period. The increased viscosity in the induction period is mainly caused by intramolecular cross-linkage reactions (Zhao and Li 1996). As the time increases, the intramolecular reaction is gradually converted into an intermolecular reaction up to the gel point. The carboxylate group ($-\text{COO}^-$) of polymers cross-links with a multi-core hydroxyl bridge ligand of Cr(III) ions, resulting in a sharp increase in viscosity. The process is the rapid cross-linking period. However, as the reaction continues, the viscosity continues to increase until the

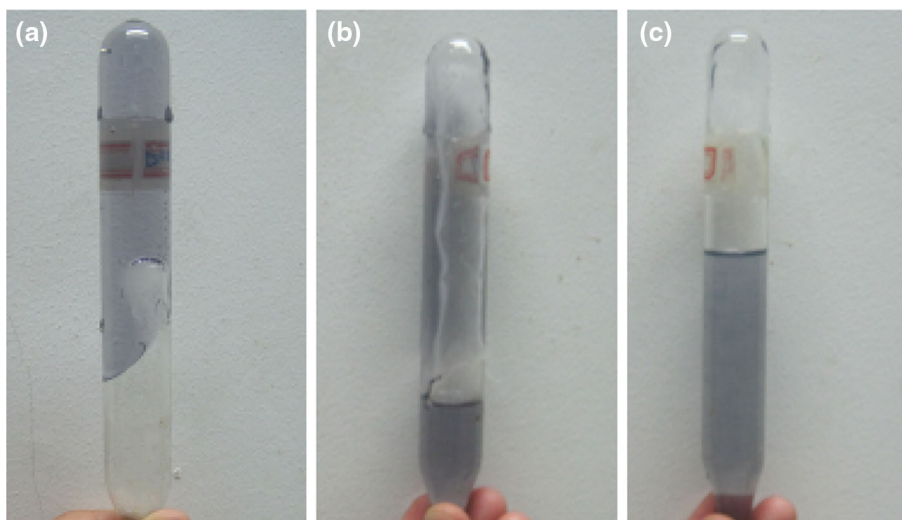
temporary plugging agent is formed. In this stabilization period, the cross-linking reaction and degradation reach dynamic equilibrium, resulting in no further increase in viscosity.

Stage II: The degradation reaction stage. A significant decrease in the viscosity of the temporary plugging agent appears. This degradation reaction stage can also be divided into three successive periods: the slow degradation reaction period, rapid degradation reaction period, and complete degradation reaction period. The viscosity changes are shown in Fig. 9. In this stage, the dynamic equilibrium between the cross-linking reaction and degradation is disrupted, and the degradation reaction begins to play a dominant role. Due to the large viscosity of the temporary plugging agent in the initial stage, less oxygen generated by ASP cannot effectively attack polymer bonds, thus resulting in a slow degradation reaction. As heating continues, more oxygen is generated and involved in the degradation, leading to a rapid reduction of the viscosity. The viscosity of the temporary plugging agent eventually decreases to 2.68 mPa s, indicating that the gel network structure has been destroyed and completely degraded. Therefore, the viscosity will not change as heating continues.

Plugging capacity and permeability recovery capacity

Figure 10 shows the plugging capacity of the temporary plugging agent at different times. The initial plugging rates

Fig. 7 Photos of temporary plugging agent in different stages. **a** Bulk gel, 2 h; **b** partial degradation, 4 h; **c** complete degradation, 6 h



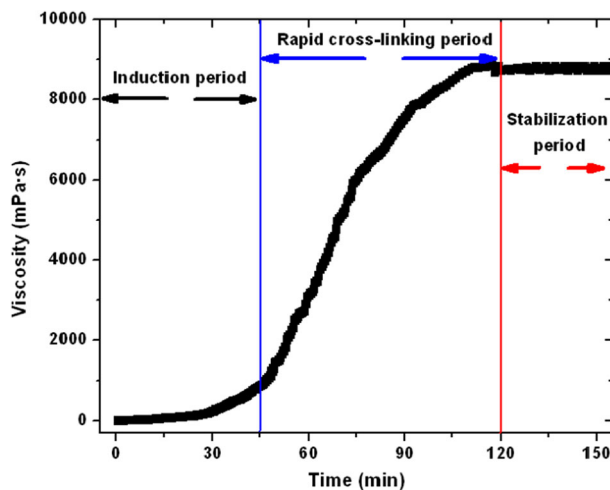


Fig. 8 Viscosity changes in cross-linking reaction stage

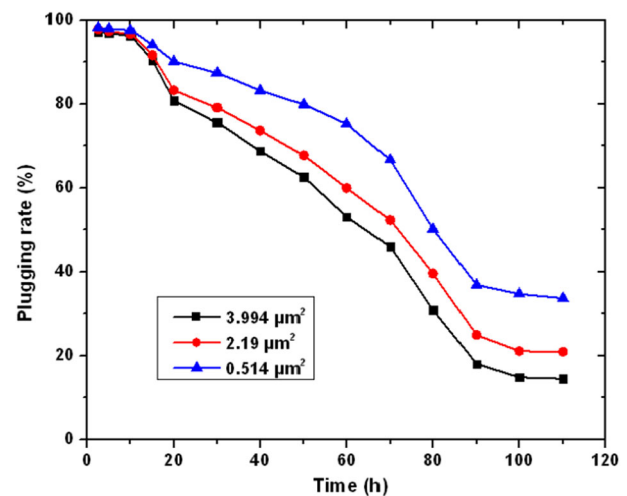


Fig. 10 Effect of time on plugging capacity

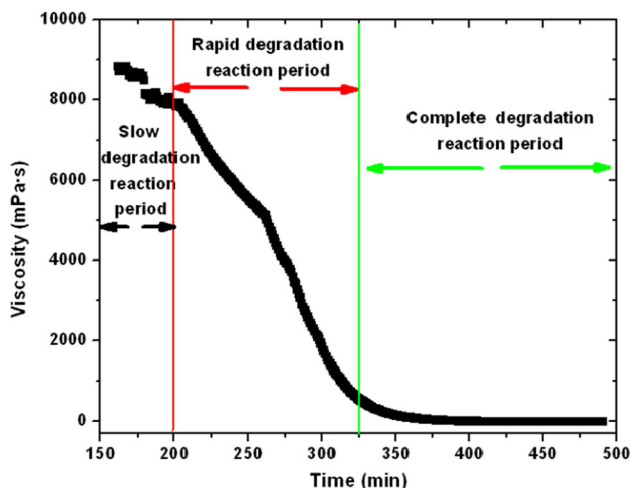


Fig. 9 Viscosity changes in degradation reaction stage

of three sand-packs were more than 97 % when the temporary plugging agent was cross-linked. This indicates that the temporary plugging agent has a good plugging capacity which can ensure that the acidizing solution enters target zones. However, the plugging rate gradually decreased with time, and finally tended to remain stable after 100 h. This can be attributed to the behavior of the temporary plugging agent in the porous media. In the initial stage, a compact three-dimensional network structure was formed¹⁷ which can bridge across the pore throats and restrict the flow of fluids, thus reducing permeability of reservoir cores. Moreover, the smaller the permeability is, the more easily the temporary plugging agent bridges across the pore throats. Therefore, the smaller permeability a sand-pack has, the larger the plugging rate. With further aging at

65 °C, APS released oxygen into solution which easily attacked the polymer bonds, resulting in an instable gel network structure in the porous media. The gel network structure was almost completely degraded after 110 h, thereby having a weak plugging capacity. The permeability recovery rates of these sand-packs were, respectively, 81.92, 75.02, and 63.42 % after 110 h which indicates that the temporary plugging agent has a good permeability recovery capacity. However, a very small amount of temporary plugging agent remained in the pores which still increased the flow resistance. As a consequence, the permeability of these sand-packs could fully recover.

Figure 11 further confirms that the temporary plugging agent has a good plugging capacity and a superior permeability recovery capacity. In the temporary plugging stage, the resistance factors of these sand-packs reached

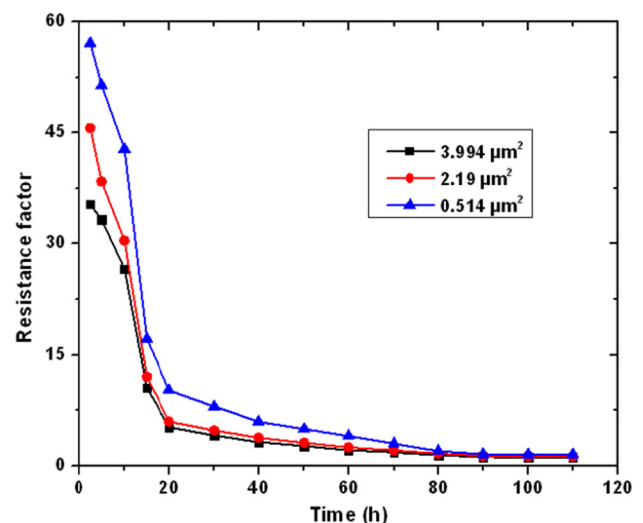


Fig. 11 Effect of time on the resistance factor

35.35, 45.63, and 57.11, respectively. This indicates that the temporary plugging agent had a good plugging capacity which increased the flow resistance in the plugging stage. However, when the acidizing treatment was finished after 110 h, the resistance factors sharply decreased to 1.15, 1.25, and 1.53, respectively. The flow conductivity of these three sand-packs increased again, and thereby, the temporary plugging agent had a superior permeability recovery capacity.

Temporary plugging capacity

Table 1 shows the overall effects of the temporary plugging agent in the acidizing process. The permeability ratios of two sand-packs were large before conducting acidizing treatment which caused injection difficult to the low permeability sand-pack. However, the permeability of the two low permeability sand-packs significantly increased after the acidizing treatment. Both the two profile improvement rates reached 69.58 and 73.43 %, demonstrating that acidizing treatment can effectively improve the formation profile. However, the temporary plugging agent is one of the most important factors in the whole acidizing process. When the temporary plugging agent was injected into the sand-packs, it preferentially entered high permeability sand-packs. By retention and bridging across the pore throats, the temporary plugging agent can effectively reduce the permeability of the porous media in the high permeability zone. Due to the small flow resistance in the low permeability sand-pack, the acid solution can easily enter without causing damage to the high permeability sand-pack. As a consequence, the permeability of low permeability sand-packs can be effectively increased. Simultaneously, the degradation of the temporary plugging agent occurs in the high permeability sand-packs. Therefore, the permeability of high permeability sand-packs gradually recovered with time. Finally, both of the two permeability recovery rates were more than 70 % which indicates that the temporary plugging agent has a good temporary plugging capacity.

Temporary plugging mechanism

Based on the above study, a temporary plugging mechanism for the temporary plugging agent is shown in Fig. 12. Due to solid-phase invasion, fines migration, scale formation, and water sensitivity, the formation near the wellbore can be easily polluted and plugged, resulting in a lower fluid production and serious heterogeneity. To enhance fluid production and improve formation heterogeneity, acidizing treatment should be conducted. To ensure the acidizing solution enters into target zones (low permeability zones) without damaging non-target zones (high permeability zones), the non-target zones should be plugged. Therefore, a temporary plugging agent must be injected into the formation before acidizing treatment. When the temporary plugging agent is injected, it preferentially enters the high permeability zones. By retention and bridging across the pore throat, the temporary plugging agent can effectively plug the high permeability zones. When injecting acidizing solution, the solution can be easily diverted into the low permeability zones, thus

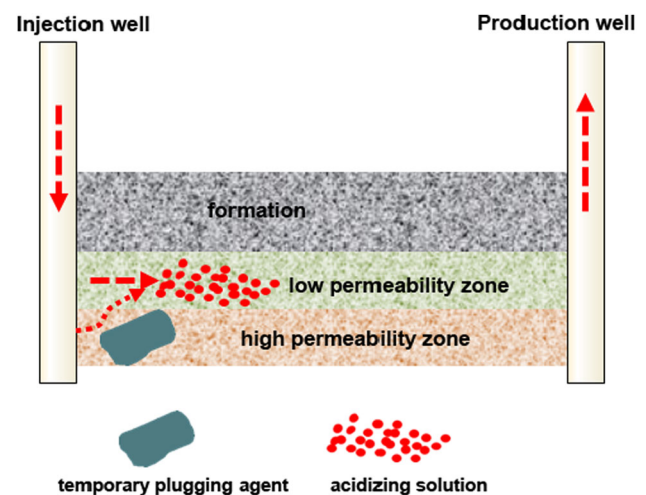


Fig. 12 Schematic of temporary plugging and acidizing process

Table 1 Temporary plugging capacity of the temporary plugging agent in acidizing process

No.	Permeability (μm^2)		Permeability recovery rate (%)	Permeability enhanced capacity	Permeability ratio		Profile improvement rate (%)
	Before treatment	After treatment			Before treatment	After treatment	
1	4.330	3.375	77.94	–	9.25	1.60	69.58
	0.468	2.106	–	4.5			
2	3.400	2.462	72.41	–	8.02	1.65	73.43
	0.424	1.490	–	3.6			

removing reservoir pollution and improving fluid production. However, degradation of the temporary plugging agent gradually occurs. The oxygen generated by APS will attack the polymer chains and lead to an instable gel network structure, and thereby, the gel strength and viscosity of temporary plugging agent are reduced. The structure of the temporary plugging agent will be completely degraded with time, and then the permeability of high permeability zones will recover. As a result, pollution near the wellbore is removed, and the permeability is improved.

Conclusions

In this work, a temporary plugging agent based on a polymer gel in the acidizing process was successfully prepared. The polymer, cross-linker, and APS concentration affect the gelation time and gel-breaking time of the temporary plugging agent. Increasing the polymer and cross-linker concentration can reduce the gelation time of the polymer gel and temporary plugging agent. However, the gelation time of the temporary plugging agent is longer than that of the polymer gel. This can be attributed to the APS in the solution. Increasing the polymer and cross-linker concentration causes difficulties in breaking the temporary plugging agent, while increasing APS concentration can generate more oxygen which makes the temporary plugging agent break easily. According to viscosity changes, the whole process can be divided into two major stages: the cross-linking stage and degradation stage. A high gel strength of the temporary plugging agent was formed in the cross-linking reaction stage which effectively plugged high permeability zones and diverted the acidizing solution into low permeability zones, whereas the degradation made the permeability of high permeability zones greatly recover after acidizing treatment. The results show that using a temporary plugging agent based on a polymer gel is an efficient way for temporarily plugging in the acidizing process.

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